

(NASA-CR-120745) SPACE PROCESSING OF
CHALCOGENIDE GLASSES Annual Report, 22 Feb.
1974 - 21 Feb. 1975 (IIT Research Inst.)
40 p HC \$3.75

N75-22344

CSCL 04A

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iITRI

IITRI Project No. D6096
First Annual Report

SPACE PROCESSING OF CHALCOGENIDE GLASS

National Aeronautics and Space
Administration
George C. Marshall Space Flight Center
Alabama 35812

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SPACE PROCESSING OF CHALCOGENIDE GLASSES

First Annual Report
22 February 1974 - 21 February 1975

Contract No. NAS8-30627
IITRI Project No. D6096

April 15, 1975

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SPACE PROCESSING OF CHALCOGENIDE GLASSES

1.0 INTRODUCTION

This project is being conducted for NASA-MSFC to investigate space processing of chalcogenide glasses. Chalcogenide glasses are good infrared transmitters and have good strength, corrosion resistance, and scale-up potential. These properties give chalcogenides promise as large 10.6 μ windows since the competition materials, alkali halides, are hydroscopic and are only available in five to six inch diameters as limited by their hot forge manufacturing technique.

The disadvantage of (earth-produced) chalcogenide glasses is that their infrared absorption coefficient is unacceptably high relative to alkali halides. It is IITRI's belief that this limitation of earth-produced chalcogenides is due to optical non-homogeneities resulting from environmental and container contamination. Processing the glass in space should improve the infrared-transmission of chalcogenides. The containerless, weightless nature of space processing should eliminate three things: 1) optical inhomogeneities caused by thermal currents and density fluctuations in the 1-g earth environment, 2) contamination from the earth melting crucible by oxygen and other elements deleterious to ir-transmission, and 3) heterogeneous nucleation at the earth melting crucible-glass interface.

The overall objective of IITRI's program is to determine the manner in which the weightless, containerless nature of in-space processing can be utilized to improve the quality of infrared transmitting chalcogenide glasses. This program is an initial effort to: 1) develop the technique of space processing chalcogenides, 2) define the process and equipment necessary to do so, and 3) predict the level of product improvement to be expected through space processing.

2.0 EARTH PROCESSING VS. SPACE PROCESSING OF CHALCOGENIDE GLASSES

The earth-bound production of chalcogenide glasses involves a five step process: 1) the elemental precursor powders are placed in a silica ampoule, 2) the ampoule is evacuated and sealed, 3) the temperature is slowly increased to the reaction temperature to form the compounded liquid, 4) the ampoule is rocked back and forth for periods up to 48 hours to homogenize the liquid, and 5) the liquid is quenched to form a glass.

The rocking of the ampoule and the resulting mixing of the liquid is necessary to overcome the micro-inhomogeneities resulting from thermal currents and density fluctuations that are due to the presence of the earth's 1-g gravity field. However, these gravity related phenomena are never completely eliminated by this method. Furthermore, this prolonged contact with the crucible material contaminates the chalcogenide with ppm levels of oxygen and other elements deleterious to ir-transmission at a wavelength of 10.6μ .

By going to space to process chalcogenide glasses both of these problems, thermal currents/density fluctuations and contamination, will be eliminated. The compounding and quenching aspects of the process can be performed in the absence of gravity, eliminating thermal convection. The zero gravity condition provides for the possibility of containerless processing, which will eliminate the contamination effects of the earth melting crucible. Thus, the weightless, containerless aspects of space manufacture has the potential for producing an improved ir-transmitting chalcogenide for use as a large diameter 10.6μ window.

3.0 RESEARCH PROGRAM

The basic concept of this program is that a mixed precursor batch can be prepared on earth and then taken to space for high temperature processing. Our initial efforts on this program have been with the arsenic trisulfide system, As_2S_3 . This chalcogenide is well characterized and is considered standard in many respects. Eventually though, we will be working with more complex systems such as $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$. This system is Texas Instrument's TI-1173 glass, and is generally considered to be the best produced on earth¹. It is anticipated that a glass exhibiting ir-transmission properties better than TI-1173 will eventually be produced in space. For these reasons TI-1173 glass was chosen as a control standard providing bench-mark data for comparative purposes.

The emphasis in our first year's effort on this program was to start to develop techniques, processes, and equipment that will eventually be used in actual in-space experiments to produce improved chalcogenides. A flow chart giving the basic elements of the first year's effort is illustrated in Figure 1. The various tasks progress through each phase of the chalcogenide production process - from the raw material stage to the melting/quenching stage.

The purpose of the blending phase of the program was to determine the optimum method of preparing a homogeneously mixed precursor powder batch on earth with minimum contamination. Liquid slurry and dry powder methods were investigated. The CVD method was not investigated in our first year's work since the small quantities of material produced by this method would not be sufficient for the various exploratory experiments conducted.

The melting phase of the program formed a large portion of our first year's effort. The emphasis here was to conduct various glass-making experiments for the purpose of determining

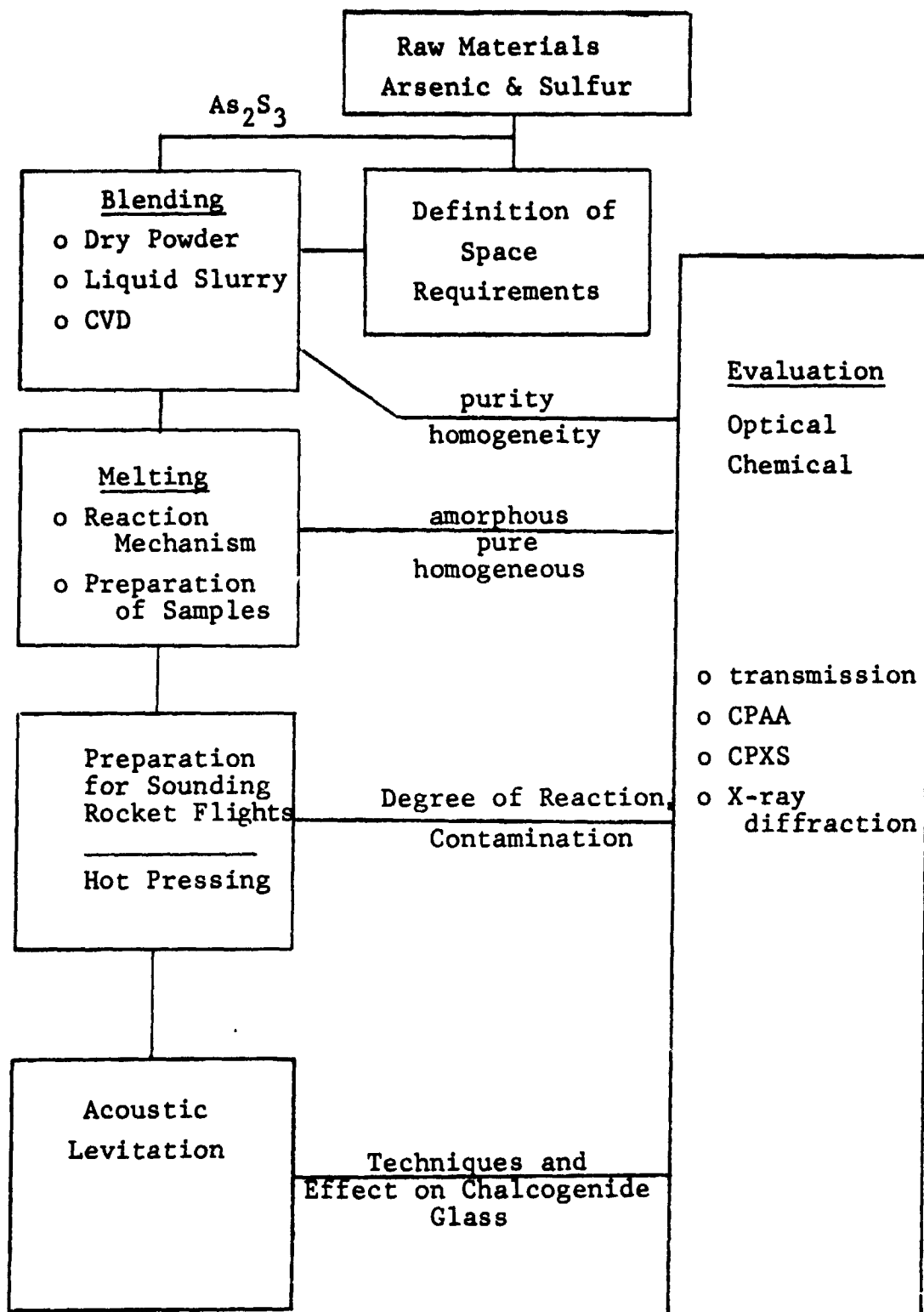
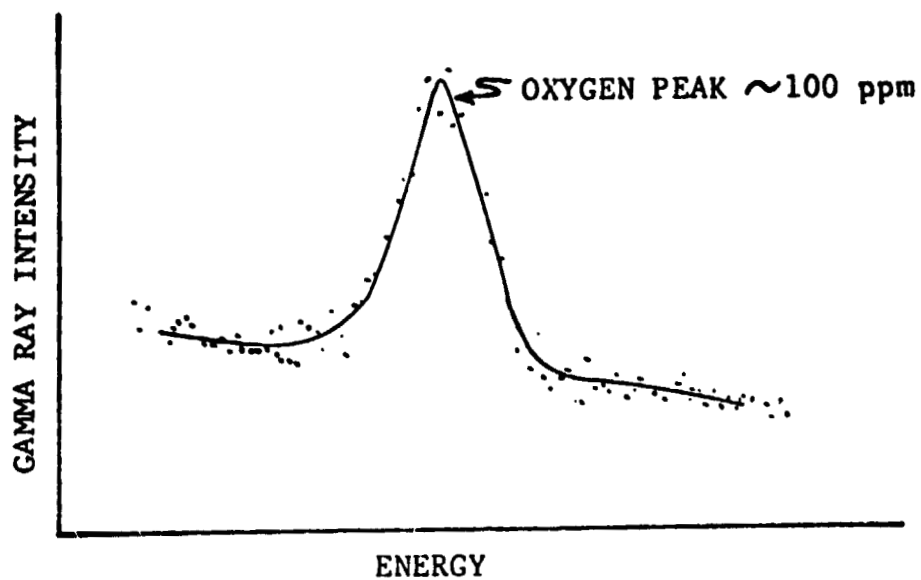


Figure 1. Flow Chart of Program

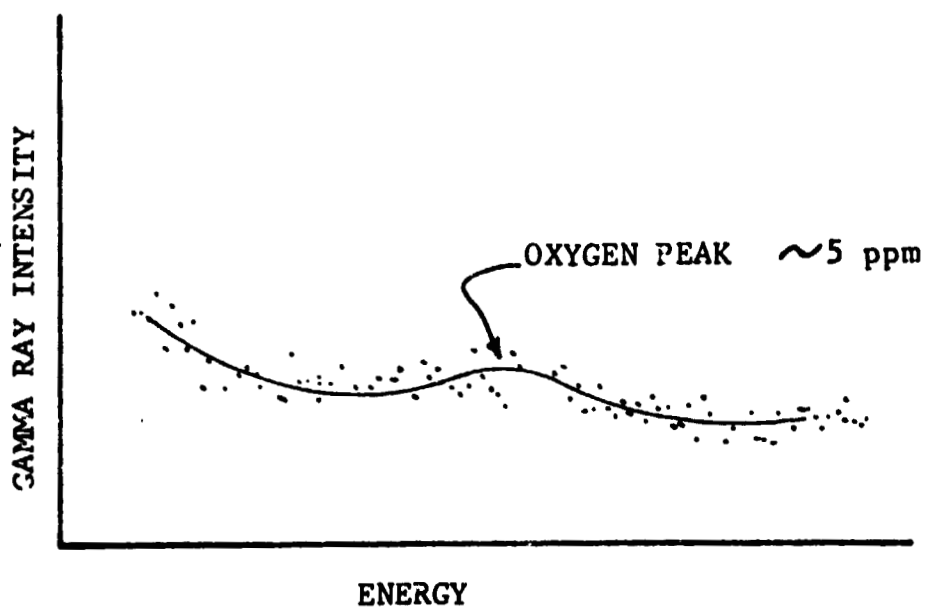
the mechanisms of reaction of the precursors. These experiments were generally conducted on cold pressed precursor pellets without rocking the furnace. This is the manner in which the actual in-space melting experiments will eventually be conducted. The ampoule-rocking that homogenizes the glass in 1-g conditions, and also contaminates the glass, will not be necessary under 0-g conditions.

The evaluation stage of the program is being conducted at various points in the chalcogenide glass production schedule. In our first year's work, for instance, we measured the ir-transmission characteristics of various glasses that were produced using an ir spectrophotometer. Additionally, we started looking at low level impurity content of chalcogenide systems. The CPAA (charged particle activation analysis) technique was employed for this purpose. Light elements ($1 < Z < 20$) undergo a variety of resonance reactions when bombarded with relatively high energy (0.5 to 2 MeV) charged particles (protons, deuterons, alphas, tritons, etc., from a Van de Graaff Accelerator). Given the bombarding charged particle and its energy, the emitted gamma radiation is characteristic of the target element. With proper calibration a measurement of the gamma-ray energies and intensities provides a quantitative measurement of the elements present in the sample subjected to charged particle bombardment. Figure 2 illustrates the results of our use of this technique to determine the oxygen content of two chalcogenides. The relative peak heights shown for the cases of 100 ppm oxygen and 5 ppm oxygen illustrates the sensitivity level of this instrument.

A large portion of our first year's effort was spent in preparation for sounding rocket flights, as indicated in the flow chart (Figure 1). This effort was not a part of our original program plan, but evolved during the course of the first year's work. Short term sounding rocket flights could be used for many preliminary space processing experiments. This approach would provide a relatively inexpensive way of learning of and



CPAA RESULTS: INITIAL IITRI CHALCOGENIDE



CPAA RESULTS: TI #1173 CHALCOGENIDE

Figure 2. CPAA Results for Low-Level Oxygen Contamination

solving many of the engineering type problems associated with space flight - e.g. effect of actual weightless conditions, effect of actual vibratory, spinning and acceleration (and deceleration) forces on the equipment/experiment, effect of instrumentation on telemetry, etc. To facilitate the processing of chalcogenide glasses under the time constraint of only six to seven minutes of low-g condition in a rocket flight, a new precursor processing technique was conceptualized - hot pressing to form a partially reacted body. Our first year's work in this area entailed initial investigations on the proper time-temperature-pressure schedules to be employed in hot pressing.

The final area of our first year's work detailed in Figure 1 is acoustic levitation. One of the major potential advantages of space for materials processing is that critical stages of the process can be accomplished without the presence of a containment vessel. The containerless aspect of space will be accomplished with the aid of levitation/position control devices that are currently under development for NASA. One such device is the Interasonics, Inc. Acoustic Levitator². Under the terms of our most recent contract amendment, this device has been made available to us. We have undertaken a cooperative effort with Interasonics to work acoustic levitation into our earth-bound chalcogenide processing experimental package. The purpose of this investigation is to investigate all of the aspects of levitation art and science and chalcogenide glass art and science to insure a high probability of success for future space processing missions. Various initial acoustic levitation experiments were conducted during the current reporting period. These experiments mainly entailed the levels of stability and control obtainable with this device.

4.0 RESULTS AND DISCUSSION

Using the As_2S_3 system we have gained much knowledge regarding the general nature of chalcogenides, and the specific constraints of in-space processing. The following sections detail the results of our experiments in the various areas outlined above.

4.1 Precursor Preparation Methods

The objective of the powder preparation phase of our program was to determine the best earth-bound method of obtaining a homogeneous mixed precursor powder batch. Mechanical mixing and liquid slurry mixing methods were investigated. The mechanical method consisted of grinding and ball-milling the as-received powders in the proper ratio. The liquid slurry method consisted of mixing the powders in an appropriate liquid to promote uniform particle dispersion, and then evaporating the liquid.

Three organic solvents were selected as the liquid vehicles for the slurry mixing experiments; acetone [CH_3COCH_3], benzene [C_6H_6], and xylene [$\text{C}_6\text{H}_4(\text{CH}_3)_2$]. The criteria considered in the selection of candidate liquid vehicles were: 1) low boiling point, 2) fast evaporation rate, and 3) good wetting properties. Acetone and benzene are well-known solvents having low boiling points ($<100^\circ\text{C}$) and high evaporation rates. Xylene also has a low boiling point ($100\text{--}200^\circ\text{C}$), but has an evaporation rate slightly lower than acetone or benzene. However, xylene exhibits good wetting characteristics and serves as an efficient dispersant.

Reagent grade arsenic and sulfur powders were used in the initial liquid slurry experiments. Two basic types of experiments were conducted. The first involved mixing both powder precursors simultaneously in a given solvent. The second involved mixing each powder separately in a solvent, and then mixing the resulting liquid solutions together. In both cases,

the final liquid solution was placed in an ultrasonic bath, and the liquid vehicle evaporated leaving well-dispersed As + S dry powder batch.

The homogeneity of the dry As + S batches prepared by the mechanical and liquid slurry conditions was then qualitatively assessed. This evaluation was made by viewing the processed batches in an optical microscope. Typical results are shown in Figures 3 and 4. Figure 3 represents a case where the mixing was mechanical and no liquid vehicle was employed. Note the large particles present which appear to be large, unmixed individual arsenic and sulfur. Figure 4 represents the case where acetone was used as a liquid vehicle. Again, a few lumps are observed. However, it is believed that these lumps are the result of caking due to the evaporation of the acetone vehicle. Agglomerated particles will not be detrimental to the liquid slurry technique if they exhibit the same homogeneity as the non-agglomerated portion of the sample.

Charged Particle X-Ray Spectroscopy (CPXS) elemental analysis was then performed on the mechanically mixed and slurry mixed samples to quantify the degree of homogeneous mixing obtained. A mechanically mixed batch and a slurry mixed batch were each sub-divided into four or five parts. Each part was analyzed for amount of elemental arsenic and sulfur present. The results are presented in terms of the ratio of the areas under the sulfur and arsenic peaks. A completely homogeneous mix would exhibit identical sulfur content/arsenic content ratios for all sections of the sample.

The results of this analysis are presented in Table I. It is illustrated that the slurry-mixed batch exhibits significantly greater homogeneity, more uniformly dispersed particles, than the mechanically mixed batch. The caked sections of the liquid slurry mixed batches possessed the same composition as the non-agglomerated sections. It can be concluded from these experiments that for space processing of an initially cold

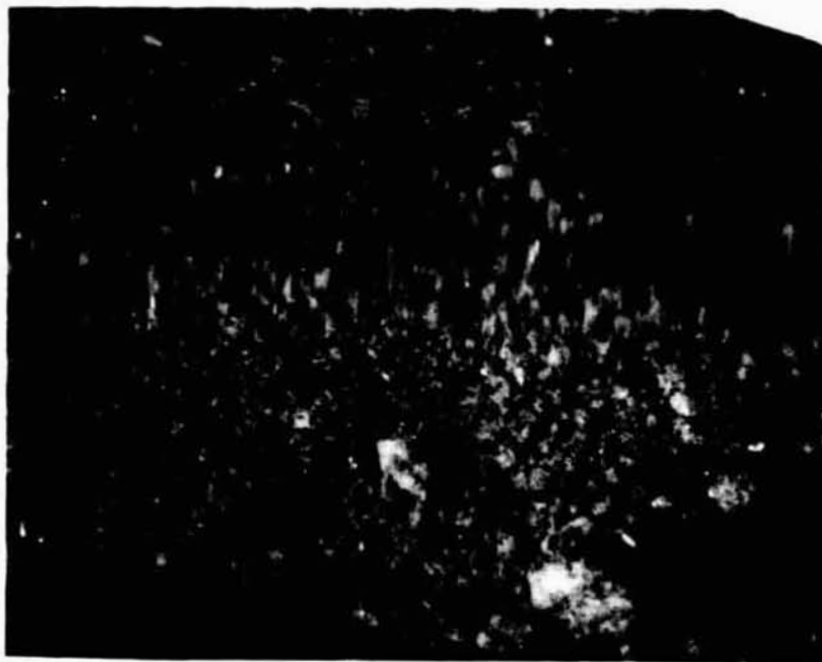


Figure 3, Optical Photomicrograph of As+S
Batch Prepared by Dry Mechanical
Mixing (25X)

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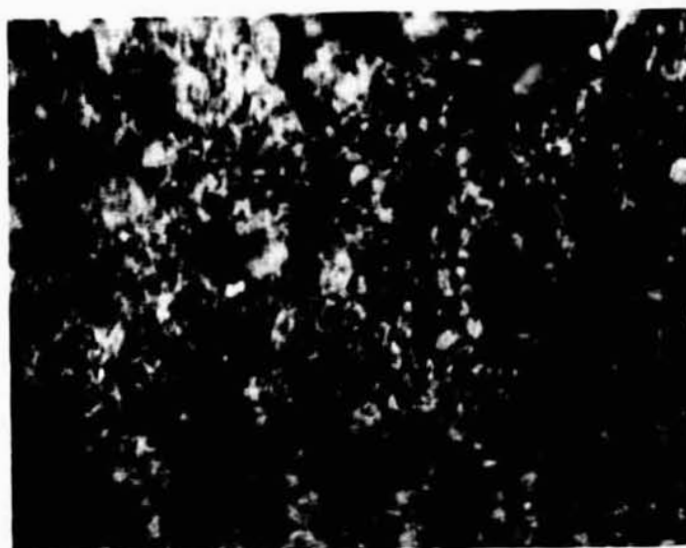


Figure 4. Optical Photomicrograph of As+S
Batch Prepared by a Liquid Slurry
Technique (80X)

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TABLE I
CPXS POWDER BATCH HOMOGENEITY RESULTS

Powder Mixing Method and Sample Number	Ratio of Sulfur Content to Arsenic Content
Mechanical #1	1.802
Mechanical #2	1.296
Mechanical #3	1.527
Mechanical #4	1.868
Mechanical #5	2.579
Slurry #1	2.189
Slurry #2	2.015
Slurry #3	2.277
Slurry #4	2.373

pressed precursor pellet, chalcogenides exhibiting better ir-transmission characteristics will be obtained if the precursor powders are prepared on earth using the liquid slurry method rather than the mechanical mixing method.

4.2 Cold-Pressed Pellet Melting

Our initial experiments in the preparation of As_2S_3 dealt with compounding the elemental arsenic and sulfur powders starting from a cold pressed pellet stage. The object of this was to determine if starting with a cold pressed batch inhibited the reaction process in any manner. Is the ampoule-rocking and resultant liquid agitation that is performed during the earth preparation of chalcogenides merely to homogenize, or is it critical in some manner to the compounding process?

To investigate this the following experiment was conducted. Starting with reagent grade sulfur powder and -325 mesh, 99.5% purity arsenic powder, a cold pressed pellet was prepared and sealed in a silica ampoule. After several attempts to determine the optimum heating schedule, the following schedule proved suitable. The precursor batch was slowly heated ($1^\circ\text{C}/\text{min}$) to $\sim 120^\circ\text{C}$ (sulfur M.P.). After a hold period at this temperature, the system was raised to the 650°C reaction temperature at $\sim 2^\circ\text{C}/\text{min}$. After a 16 hour hold period at 650°C (with no rocking to homogenize) the reacted liquid was quenched to form the glass, and subsequently annealed.

Figure 5 is a photograph of the processed chalcogenide and ampoule. Note the small amount of sulfur condensed on the upper part of the ampoule. This phenomenon will be accounted for in subsequent experiments dealing with the stoichiometry of the compounded glass.

Figure 6 illustrated the ir-transmittance of As_2S_3 produced in this manner (i.e. from a cold pressed pellet) as a function of wave length. Figure 7 illustrates the ir-transmittance of a commercially available As_2S_3 produced on

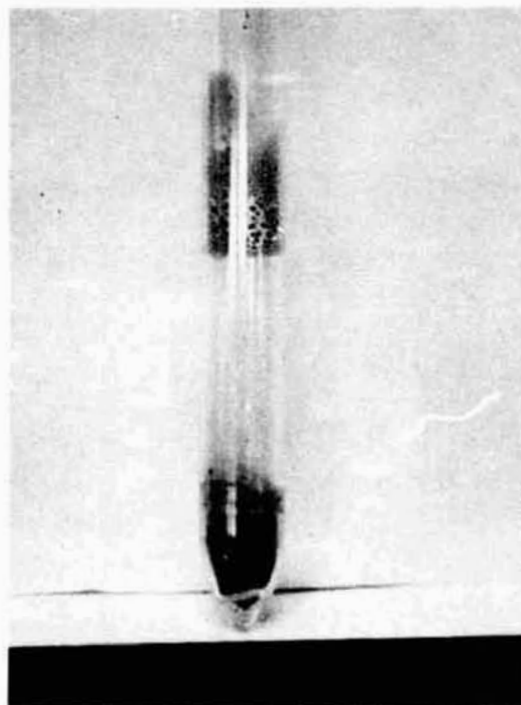
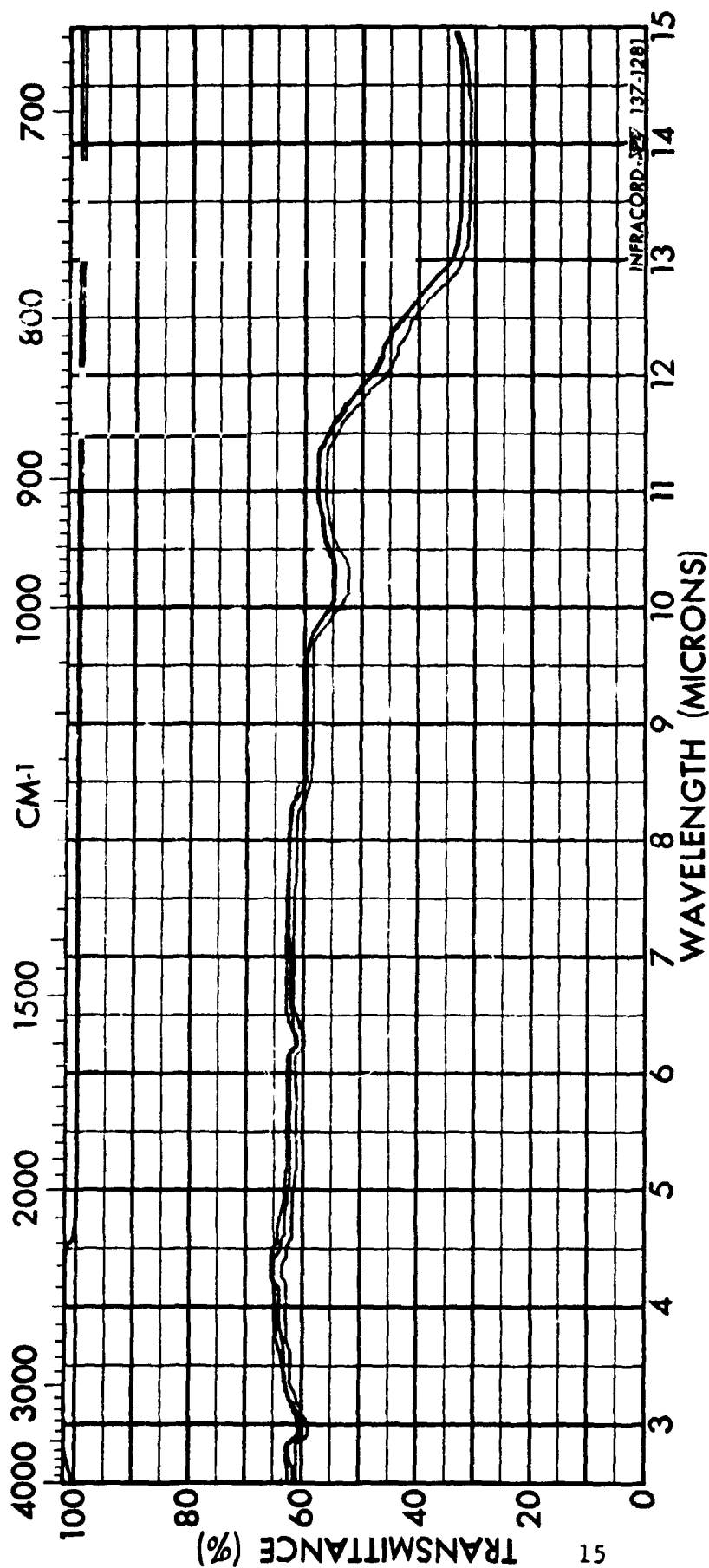


Figure 5. Photograph of Processed Chalcogenide and Ampoule

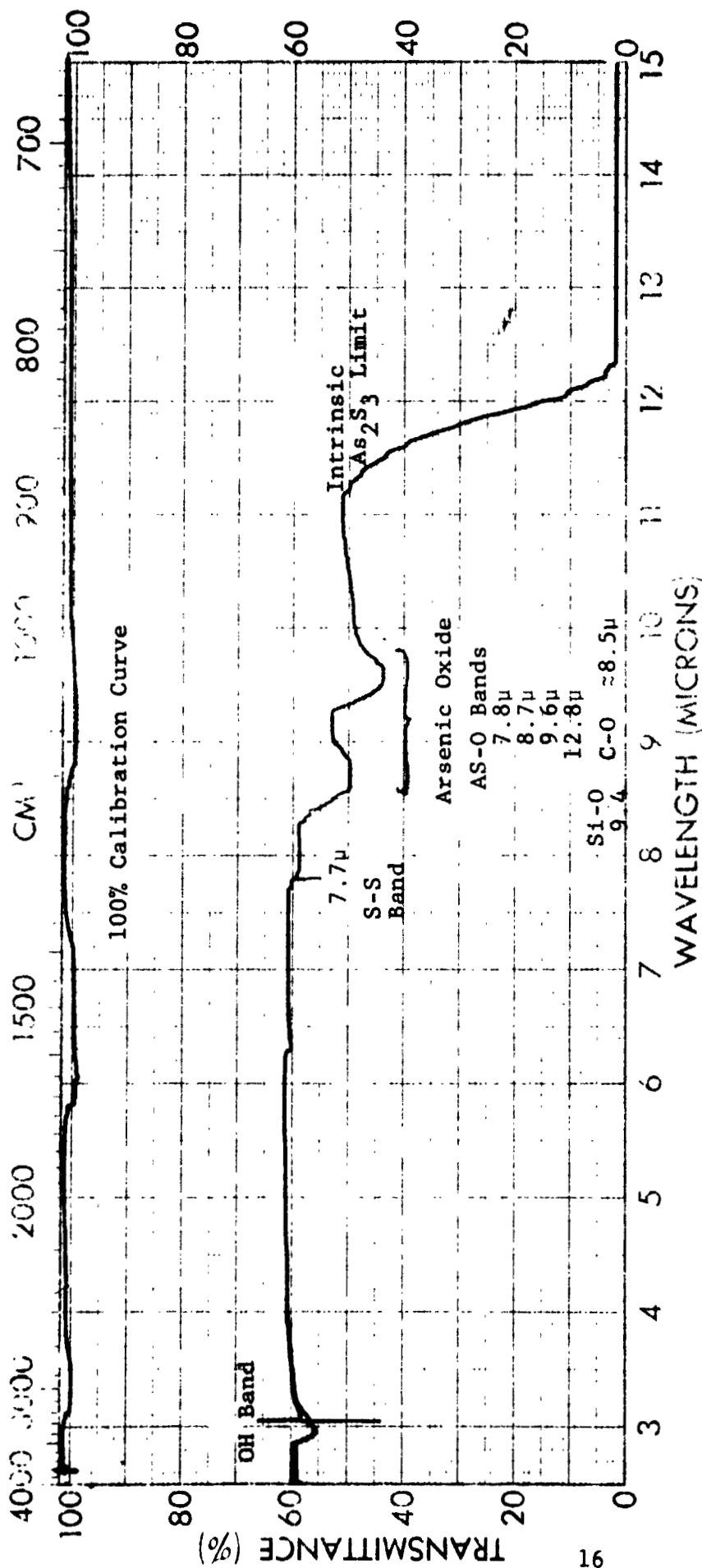
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SPECTRUM NO. _____
SAMPLE _____

SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE As_2S_3 (99.5% Arsenic, lab grade sulfur)	Color: slightly reddish brown	Sample Size = .42 x .39 inch	Small sample size; small
Cold Pressed Pellet Melted in Sealed Ampoule	PURITY	2.	particle of unmelted
(BDR-11)	PHASE	DATE 5/29/74	arsenic in sample.
	THICKNESS 0.088 inch	OPERATOR MAA	

Figure 6. Infrared Transmittance of As_2S_3 Processed from a Cold-Pressed Pellet



16

SPECTRUM NO. _____
SAMPLE _____

SPECTRUM NO. 1	ORIGIN	LEGEND	REMARKS
SAMPLE As_2S_3		1.	In sulfur rich glass
Commercial Material	PURITY	2.	the S-S bands are lo-
	PHASE	DATE 9/10/74	cated at 7.7 μ , 10.15 μ
	THICKNESS	OPERATOR <i>W. J. or</i>	and 11.9 μ .

Figure 7. Infrared Transmittance of Commercial
PART NO. 137-1281 As_2S_3 Glass.

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

earth. The rough similarity of the transmission characteristics of these two samples leads to the conclusion that our concept of producing chalcogenides from cold pressed precursor pellets is valid.

4.3 Preparation for Sounding Rocket Flights

Having gained some knowledge regarding the mechanisms of reaction of chalcogenide precursors, we turned our attention to the constraints of space manufacture and particularly the constraints of NASA's Space Processing Program which we have to work within. We have learned that a successful reaction of mixed As + S powders via a solid-liquid reaction in a sealed container requires relatively long heating times (hours). This is due mainly to melting point differences and vapor pressure considerations for the constituent elements. Ideally, we would like, however, to be working with materials systems that required heating times in minutes rather than hours. If we had such a system we could do many preliminary space processing experiments in sounding rockets, for instance.

For these reasons we have conceptualized a preparation technique for As_2S_3 that might reduce the in-space processing times considerably. This preparation technique involves hot pressing the precursor powders. The reasoning proceeds as follows. In a sealed container where arsenic and sulfur powders are reacted, the melting point disparity (120°C for sulfur, $>600^\circ\text{C}$ for arsenic) dictates that heating is done slowly so that the solid arsenic can react with the liquid sulfur. Sulfur is kept in the liquid state by its own vapor pressure above the melt. Too rapid heating will cause the pressure above the melt to rise to a level sufficient to fracture the SiO_2 container before the arsenic is fully reacted. The general idea of our hot pressing concept is to provide the pressure necessary to keep the sulfur molten while still in the low temperature, highly viscous sample preparation stage (i.e. on earth).

This will produce a partially reacted sample that will withstand the forces of liftoff better than a cold pressed pellet. The final high temperature reaction to form As_2S_3 will be accomplished in a relatively short time in space (hopefully minutes instead of hours), and thus be amenable to preliminary sounding rocket experiments.

Our initial hot pressing experiments were aimed at determining the feasibility of the hot pressing concept, and to get a rough idea of the temperature, pressure, and time boundaries we have to work within for this concept to be successful. The feasibility of partially reacting arsenic and sulfur powders by hot pressing was investigated utilizing the apparatus illustrated schematically in Figure 8. The precursor powders were contained within the graphite mold/plunger system. This system was heated with a wire-wound heater, and inserted into a standard Instron testing machine. The upper graphite plunger was connected to the upper (movable) Instron crosshead. The force necessary to deform the plunger was monitored with a strain gage type load cell.

Several initial hot pressing experiments were conducted. The variables studied were temperature, pressure, and time. Temperatures ranged from 100° to 400°C . Pressures ranged from 500 to 2000 psi. Hot pressing times ranged from 15 to 30 min. It was found that for temperatures less than 200°C for pressures ranging from 500 to 2000 psi, the hot pressed product appeared visually as relatively unreacted powders, similar to the visual appearance of a cold pressed $\text{As} + \text{S}$ pellet. For processing temperatures between 250° and 400°C , at any pressure from 500 to 2000 psi, much material was extruded at the upper plunger-mold wall interface. The extrusion appeared high in sulfur and presumably was due to the rapid volatilization of the sulfur precursor.

However, at a temperature of 200°C with an applied pressure of 2000 psi minimum extrusion occurred. A section

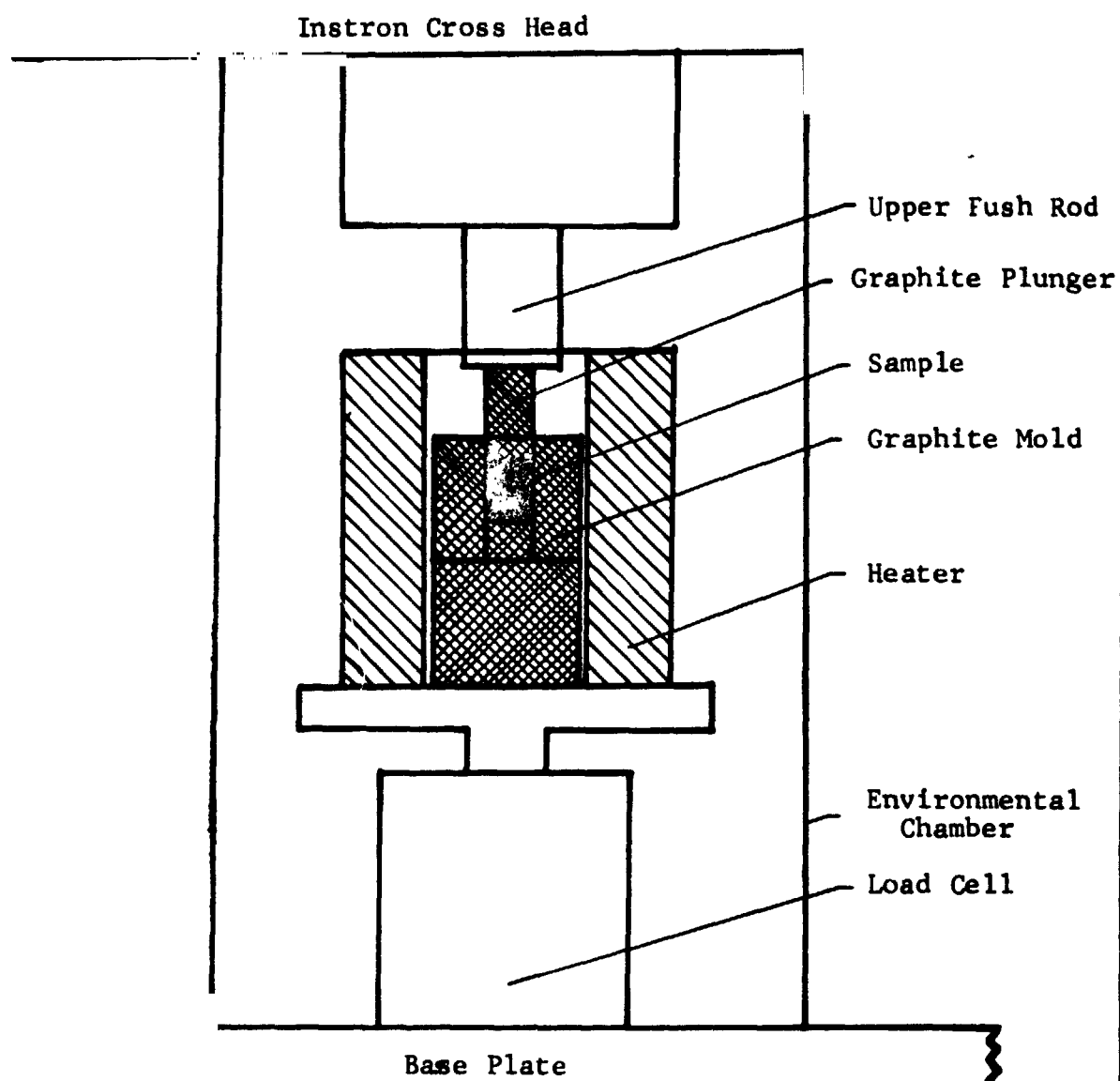


Figure 8. SCHEMATIC OF CHALCOGENIDE GLASS PRECURSOR PROCESSING EQUIPMENT

of the mold-plunger-sample system is shown in Figure 9. Upon removing and polishing, the hot pressed sample appeared distinctly metallic, a rough qualitative indication that significant As + S reaction had occurred.

This sample was submitted for CPAA analysis. The first result of this analysis was that the arsenic to sulfur ratio for this hot pressed material was similar to that of a commercially available As_2S_3 glass analyzed by CPAA. The second result of the CPAA analysis on the hot pressed As + S sample was that significant carbon contamination was present at a depth of a few microns. This contamination is presumably related to diffusion from the graphite mold employed. To eliminate this problem subsequent hot pressing experiments were conducted in a stainless steel system.

At this point, an additional variable, time, was added to our As + S hot pressing experiments. Following the 200°C, 2000 psi schedule that gave promising results in our initial experiments, additional batches were hot pressed for times up to a few hours. No apparent differences in these samples processed for varying times were visually observed.

In order to more quantitatively assess the quality of the hot pressed samples that visually appeared to have undergone a significant $2\text{As} + 3\text{S} \rightarrow \text{As}_2\text{S}_3$ reaction, X-ray diffraction analyses were conducted to indicate the amount of crystallinity present. The precursor arsenic powder is crystalline. Thus a comparison of X-ray analyses of a mixed As + S powder batch prior to hot pressing with a hot pressed pellet should provide a qualitative indication of the degree of chemical reaction obtained by hot pressing. After chemical reaction the arsenic should be relatively amorphous. Thus, a significant drop in crystallinity should be observed in our hot pressed samples. This evaluation technique can be made semi-quantitative, in a comparative sense. For instance, changes in the hot pressing

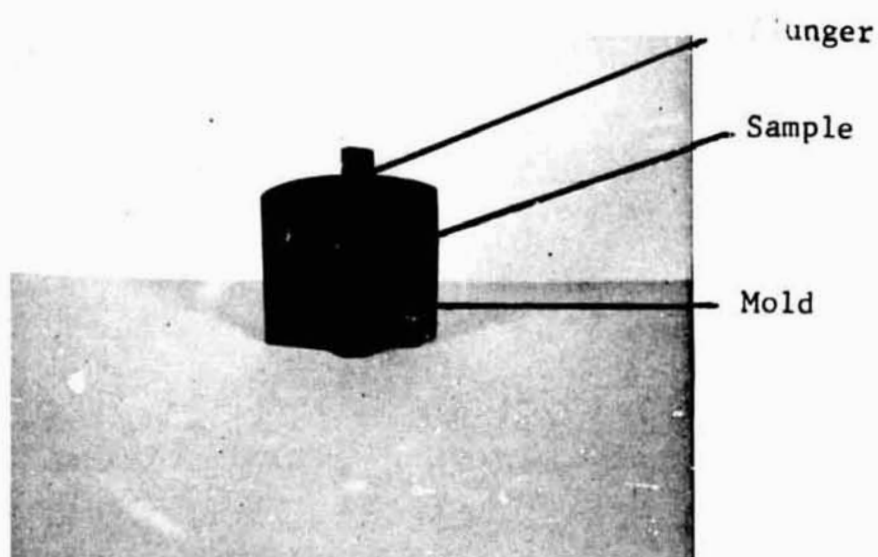


Figure 9. Sectioned View of Hot Pressed Arsenic
And Sulphur Precursors

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schedule can be quantified by assignment of a number corresponding to, say, the area under the arsenic peak or the height of the arsenic peak in a diffraction pattern.

This analysis was applied to our "best" preliminary hot pressed sample (200°C, 2000 psi) with results shown in Table II. This semi-quantitative result indicates that although our initial hot pressed samples appeared significantly glassy, there remained a substantial amount of unreacted (crystalline) arsenic. This result indicates that the time-temperature-pressure hot pressing schedule must be altered in a manner to promote more complete reaction.

Further hot pressing experiments were conducted at higher temperatures and pressures to promote more complete reaction. These experiments invariably lead to much extrusion of the low melting sulfur at the upper plunger-mold wall interface. To circumvent this problem, other time-temperature-pressure schedules were investigated. For instance, for hot pressing similar materials with widely different melting points, La Course³ has found it convenient to use the following schedule: 1) slowly raise the temperature to slightly above the lowest M.P. in the system (120°C for sulfur in our case) with no applied pressure, 2) slowly raise the temperature to the desired pressing temperature, and 3) apply the desired pressure. Presumably, this schedule permits the formation of a relatively thick colloidal solution that will not extrude easily before the arsenic is completely reacted. Additionally, this schedule provides for better pressure control as the sulfur volume rapidly increases during the ring-to-chain structure transformation.

4.4 Acoustic Levitation

The Intersonics acoustic levitation/position control device is pictured in Figure 10. The basic operation of this device is that an acoustic force field is established within

TABLE II

X-RAY ANALYSIS OF VIRGIN AND HOT PRESSED As+S BATCHES

Sample	Number Indicating Relative Height of Arsenic Peak
1. Virgin As+S Precursor Powder Batch	79
2. "Best" Preliminary Hot Pressed Sample	71

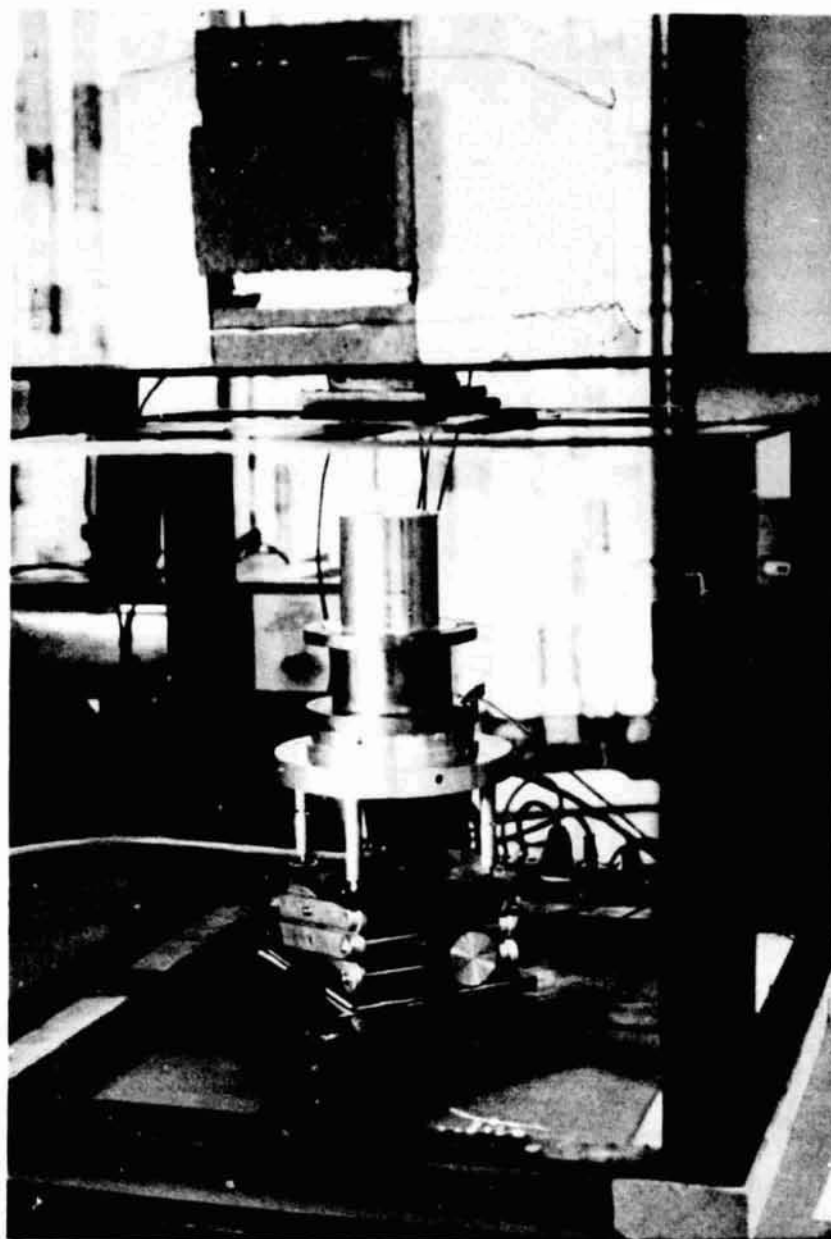


Figure 10. Photograph of Intersonics
Acoustic Levitator

the containment cylinder (Figure 11) and the sample material is constrained to holes (energy minimums) in the sound field. The high temperature process is performed in the furnace region of the tube. The sample is then moved to a cooler portion for quenching (Figure 11).

R. R. Whymark of Intersonics and IITRI personnel installed the equipment. Experiments were then conducted wherein various materials were levitated at ambient room temperature to gain experience with the device and to investigate the level of stability and control attainable.

Initial experiments were conducted with low density styrofoam spheres up to several millimeters in diameter. Excellent stability and control was obtained with this low density material. Levitation was successfully conducted for periods up to 90 minutes, which provides a good indication of the potential of this system for making glass melting experiments in space.

The next series of levitation experiments were conducted using 5 mm diameter, 2 mm thick polystyrene discs. Levitation was accomplished for periods up to 20 minutes. However, it was difficult to maintain stable levitation without the sample spinning. Under these conditions of 1-g levitation, the main drive coil of the acoustic levitator frequently burned out. In an attempt to eliminate this problem, convective cooling was applied to the coil area.

The addition of convective cooling permitted operation at higher power levels. Several levitation experiments were conducted with 3-5 mm diameter soda-lime glass beads. With the unit operating at maximum power (determined by a maximum permissible current density for the 24 gauge wire of the main drive coil) a glass bead could be levitated only for short periods (few seconds). For our earth-bound processing experiments to be successful, we will need more stability, control,

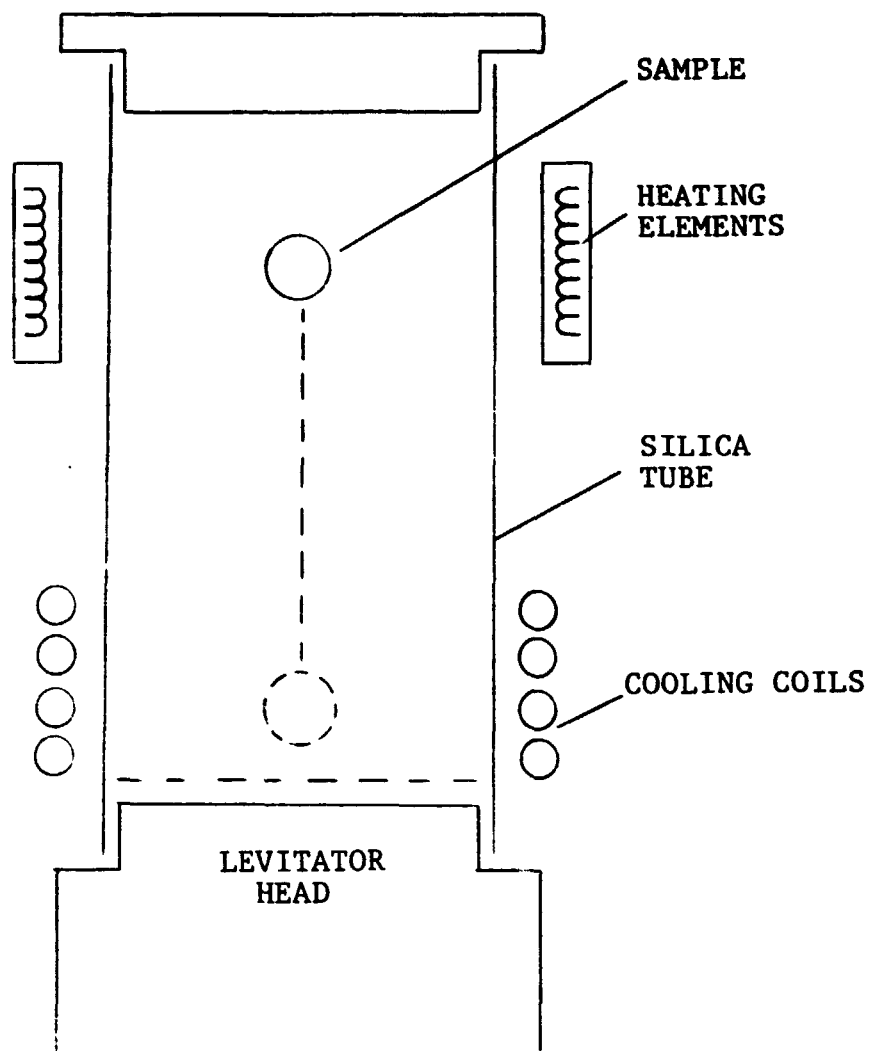


Figure 11 Levitation Melting

and time than has been obtained in these glass bead levitation experiments. R. R. Whymark is currently experimenting with higher power drive coil designs to eliminate this problem.

In the weightless in-space environment, however, much lower power levels will be required for levitation since the earth's 1-g gravity force will not be acting on the sample materials being levitated. An indication of the power levels required under near-zero-g conditions will be obtained when the results are collected and analyzed from the recent drop tower testing that Intersonics has conducted at NASA-MSFC.

At the conclusion of this reporting period the equipment is being used for the Intersonics drop tower tests. Our experiments with the acoustic levitation will continue when this work is completed.

5.0 CONCLUSIONS

During this phase of the work effort with the As_2S_3 system, we have gained experience about the general behavior of ir-transmitting chalcogenides, as well as the nature of the necessary constraints of the in-space experiments. For instance, not only are we dealing with the basic materials science of the As_2S_3 system, we have incorporated acoustic levitation into our experimental package as well. Here we are investigating all of the trade offs that are involved (e.g., processing temperature-time schedule, evolved gas species, pressure gradients, temperature gradients, heating methods, levitation control and stability, etc.). The concept here is that our earth-bound experiments will demonstrate that all the compatibility conditions and constraints of in-space processing are satisfied. The use of a levitation or position control device has been integrated into our work with the As_2S_3 system. In this manner we can work towards confidence that early in-space processing experiments will be successful.

Several conclusions have been reached during this phase of the program. They are outlined as follows:

- A. The concept of going to space with a cold-pressed pellet is valid, as long as we can achieve a high degree of homogeneity in our earth-mixed precursor powders.
- B. A highly homogeneous cold pressed pellet can be prepared on earth using the liquid slurry method of particle mixing. This method was shown to be greatly superior to the mechanical dry mixing method.
- C. It has been determined that the concept of hot pressing the precursor powders to reduce the time necessary for higher temperature processing appears feasible. However, much work will be required

before we are ready for a sounding rocket flight. It is our belief, however, that this work should be de-emphasized in the future. The most promising route to improve chalcogenide glasses will be through the utilization of future manned orbital flights that do not have the constraint of only 6 - 7 minutes of weightlessness that exists in a Sounding Rocket flight. Sounding Rocket experimentation will provide valuable engineering-type information, but it is highly doubtful that an improved chalcogenide will be produced in any such flight. It is IITRI's belief that the 6 - 7 minute time constraint of a Sounding Rocket flight is much too stringent to permit the production of improved chalcogenides. More time is needed due to the melting point differences of the constituent elements. This problem will be partially eliminated by hot pressing the precursors, but at the sacrifice of increased contamination.

- D. The addition of the Intersonics Acoustic Levitation/ Position Control Device to our experimental package permits us to investigate all of the trade-off aspects of our chalcogenide glass production prior to an actual space flight. In this manner the facility and the experiment can be developed together to insure a high probability of success for early missions. A higher power drive coil than is currently supplied with the device will be required for stable, long time 1-g levitation. However, this will not be a limitation under actual low-g conditions, since power requirements will be lower by several orders of magnitude. Additionally, many useful 1-g experiments can be conducted with the aid of a small minimum contact stinger such as a wire.

- E. Much knowledge has been gained regarding the processing of As_2S_3 glass relative to the constraints of space manufacture. However, it is recognized that initial space processing flights will be most meaningful if we use a chalcogenide glass that is considered to be the best produced by conventional earth methods. This glass is Texas Instrument's $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ chalcogenide (TI-1173). Our future earth experiments are thus designed around this composition, using our experience with As_2S_3 as a base.
- F. During the course of working with the acoustic levitation device, we became aware of a phenomenon that has great potential for increasing the homogeneity of the chalcogenide glass while maintaining a very high degree of purity. This technique will be explained in detail in the following section. Essentially this technique entails a form of non-contact mechanical mixing that can be performed with the acoustic levitation device by rhythmic variations in the sound field intensity.

6.0 FUTURE WORK

Work during the next twelve month period on this program will be conducted with two chalcogenide systems, As_2S_3 and $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$.

6.1 As_2S_3 Glasses

When the Intersonics Acoustic Levitation device is returned to IITRI, we will initiate a series of levitation experiments with As_2S_3 glasses. Until a higher power drive coil is available for earth levitation, we will be using a stinger to help hold the glass in position in our experiments. Use of a stinger will greatly aid our earth experiments and will provide minimal contamination since only a small portion of the sample will be in contact with the stinger. Ultimately, however, improved chalcogenides will be processed in space under truly containerless conditions.

The first series of experiments to be conducted will be the melting of commercial As_2S_3 glass on a stinger in the levitation chamber (with the sound field on). We will be investigating heating and cooling methods, stability and control at high temperature ($\sim 300^\circ\text{C}$), evolution of gases, etc. Many of the aspects of our high temperature process that could effect levitation will be studied.

The next series of experiments will involve our "massaging the melt" concept of homogenization. This concept was discussed at the recent project review held at NASA-MSFC, and entails deforming the molten sample in a cyclic manner while being levitated (a phenomenon that has been observed by Whymark (2)). This should promote non-contact homogenization of the melt and will replace the contaminating rocking-ampoule method used in earth-bound chalcogenide processing. These earth experiments will also be conducted with the aid of a stinger, and will entail determining how the sound field intensity can be varied to change the shape of a low viscosity material being supported by

a stinger. Eventually, equal mass precursor powders will probably be required for this, and contamination and homogeneity obtained will be compared with conventional methods.

Another series of experiments will entail processing of cold pressed precursor pellets on a stinger (such as wire) while in the acoustic environment. These series of experiments combine all of the aspects of the chalcogenide production process and acoustic levitation. Variables to be studied will include 1) reaction kinetics, 2) stoichiometry of the glass product relative to precursor composition, 3) effect of evolved gas species on levitation, 4) optimum gas pressure for the process, 5) container to sample volume ratio, 6) effect of minimal container contact - all of the trade-offs between chalcogenide glass science, and the levitation mechanism that will effect the quality of the space-produced chalcogenide.

When a higher power drive coil becomes available that will facilitate long-time levitation under 1-g conditions, the above experiments will be repeated without a stinger (i.e., under truly containerless conditions).

6.2 Ge₂₈Sb₁₂Se₆₀ Glasses

Ge₂₈Sb₁₂Se₆₀ glass (Texas Instrument's TI 1173) is the major subject of our next year's effort. This glass is generally recognized as the best 10.6 μ chalcogenide produced on earth (1). Our work with this glass will generally follow along the lines of our experiments with As₂S₃. The precursor germanium, antimony, and selenium materials will be suitably treated to remove absorbed surface impurities. Texas Instruments has found that this can be accomplished by passing a suitable reactive gas, such as hot hydrogen, over the surface of the precursor materials. Similarly, all silica ware will be pre-treated by etch and heat treatment. Mechanical and liquid slurry mixing techniques will be investigated for the purpose of obtaining a homogeneously mixed precursor batch. Acoustic levitation experiments similar to those described above will be conducted also.

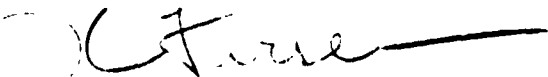
In view of the conclusions we have reached regarding hot pressing experiments, and the general idea of using sounding rockets experimentation to our advantage, we intend to conduct only a limited number of hot pressing experiments with $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ materials. The purpose of these experiments will be to determine if a suitably reacted precursor batch (i.e., reacted enough for a successful sounding rocket flight) can be obtained with much less difficulty than we have previously experienced with the As_2S_3 system. The rationale for this approach is that LaCourse (3) has experienced much less difficulty in hot pressing the arsenic selenide system than we have in trying to hot press the As_2S_3 system. Presumably, the elimination of sulfur has made the system much more amenable to hot pressing.

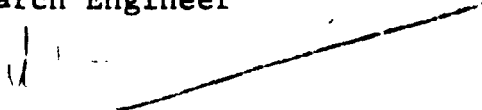
7.0 CLOSURE

Based on the results and conclusions of the initial work phase of this program, it is our belief that progress has been made in the area of space processing of chalcogenide glasses. We are looking forward to continuing with this work in the next phase of our program.

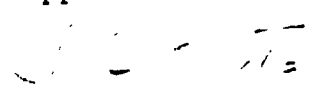
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REFERENCES

1. Segawa, D.K., "8 to 14 Micron Infrared Fiber Optics," AFAL-TR-68-16, March 1968.
2. Whymark, R.R., "Acoustic Field Positioning for Containerless Processing," "Proceedings Third Space Processing Symposium - Skylab Results," NASA-MSFC, May 1974.
3. La Course, W., Alfred University, private communication.